On the Interplay Between Force, Temperature, and Electric Fields in the Rupture Process of Mechanophores

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Abstract

The use of oriented external electric fields (OEEFs) shows promise as an alternative method for catalyzing chemical reactions. The ability to target a specific bond by aligning it with a bond-weakening electric field may be beneficial in mechanochemical reactions, which use mechanical force to selectively rupture specific bonds. Previous computational studies have focused primarily on a static description of molecules in OEEFs, while the crucial influence of thermal oscillations on the stability of the molecules has been neglected. Here, we performed ab initio molecular dynamics (AIMD) simulations based on density functional theory (DFT) to investigate the behaviour of a model mechanophore under the simultaneous influence of thermal and electric field effects. We examine and compare the changes to the bond and its thermal oscillations in strong OEEFs at various temperatures, without and with mechanical stretching forces applied to the molecule. We show that the change in bond length caused by an electric field is largely independent of the temperature, both without and with applied mechanical force. The amplitude of the thermal oscillation increases with increasing field strength and with increasing temperature, but at low temperatures, the application of mechanical force leads to an additional increase in amplitude. Our research shows that methods for applying mechanical force and OEEFs can be safely combined and included in an AIMD simulation at both low and high temperatures, allowing researchers to computationally investigate mechanochemical reactions in realistic application scenarios.

1 Introduction

Oriented external electric fields (OEEFs) have established themselves as a focus of research into alternative forms of chemical catalysis.[1,2] By selectively stabilizing transition states that would be unfavourable under other conditions, OEEFs can enable unlikely reaction pathways.[3,4] In addition, the application of an OEEF allows for control over both reactivity and selectivity of various chemical reactions,[1,5–9] and, while far from straightforward experimentally, adjusting the strength and alignment of the OEEF with the molecule allows controlling the outcome of the reaction.[2,6,10]

While computational studies utilizing OEEFs have become increasingly common,[5–7,11–15] a newer field of interest for the potential applications of OEEFs is mechanochemistry,[16] particularly the reactivity of mechanophores. Mechanophores are molecules that react to mechanical stress.[17–19] They typically have a specific bond known as the scissile bond, which ruptures when enough mechanical force is applied, causing structural changes within the molecule. These changes can have various effects, from changing the substance's colour[18,20] to releasing small molecules from the structure.[19,21–23]

In a previous computational study,[24] we investigated the effects that the combination of OEEFs and mechanical force has on the structure of mechanophores. We found that the bond-weakening effects of these two external properties can amplify each other depending on their relative orientation. The investigation was done using relaxed ground state electronic structure calculations, but any practical application of this combined approach would also need to consider the system's temperature and its effect on the molecular geometry of a mechanophore. A computational study that considers the effect of temperature on a mechanophore would use molecular dynamics (MD) simulation methods to describe the evolution of the molecule's geometry over time. Specifically, the use of *ab initio* molecular dynamics (AIMD)[25] is a well-established option for investigating the behaviour and reactivity of mechanophores in a thermal environment.[26,27] In AIMD, the electronic structure of the system is calculated at each time step using electronic structure methods such as density functional theory (DFT).[28,29] While this enables the accurate description of the electronic changes caused by the application of mechanical force as well as OEEFs throughout the simulation,[26,30,31]

no computational study exploring the influence of temperature on the behaviour of a strained mechanophore in an OEEF has been done until now.

In this work, we use a small model mechanophore to investigate how the influence of mechanical force and electric field on a scissile bond's geometry changes at different temperatures. Using AIMD simulations based on DFT, we explore the changes in the bond length as well as the thermally induced vibration of the mechanophore's scissile bond at different temperatures in static OEEFs. We compare the effects without and with mechanical stretching force applied along the molecule. Our goal in this work is to show how much the effects of OEEFs and mechanical force on a mechanophore's geometry change with the system's temperature, and how much the effects of temperature change with the OEEF. Additionally, we show that AIMD simulations can be used to combine the effects of OEEFs, mechanical force, and temperature to form a comprehensive model for investigating the behaviour of a mechanophore in a realistic application scenario.

The rest of this work is structured as follows: In section 2, we present the methodology of our investigation and the computational methods we used for it. In section 3, we discuss the behaviour of our model system at different temperatures and electric field strengths, both with and without mechanical force. Conclusions and outlook are given in section 4.

2   Computational Details
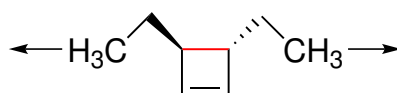
Figure 1: *Schematic representation of the model mechanophore. The scissile bond is shown in red. The methyl groups to which mechanical forces are applied are indicated by arrows. The direction of the arrows coincides with the direction of the OEEF.*

For this work, we investigated a cyclobutene with minimal linkers (Figure 1). Cyclobutene derivatives are mechanophores with a scissile $C-C$ bond that perform ring opening when mechanical force is applied.[32–34] The small size of the model structure allowed us to perform large-scale simulations.

Electronic structure calculations were performed using Q-Chem 6.1.1[35] at the ωB97X-V/cc-pVDZ level of theory,[36,37] which has been shown to provide good accuracy when simulating organic molecules in strong electric fields.[38]

We investigated the influence of an OEEF on the scissile bond under thermal conditions. To achieve this, we performed single-molecule Born-Oppenheimer Molecular Dynamics (BOMD) simulations.[25] Each simulation calculated 11,000 time steps at 0.484 fs per time step, for 5.324 ps of total simulation time. Simulations were performed at constant thermal energy by assigning initial atomic velocities using Maxwell-Boltzmann sampling. Simulations were performed at temperatures between 60 K and 600 K in steps of 60 K.

In this work, electric field strength is given in atomic units (1 a.u. ≈ 51.4 V Å^{-1}). During the simulation, external electric fields between 0.00 a.u. and 0.05 a.u. in steps of 0.005 a.u. were applied along the stretching coordinate indicated by arrows in Figure 1. To apply the OEEF, we used a custom routine that always aligned the electric field with the marked atoms during the simulation. For each combination of simulation temperature and electric field strength, ten simulations were performed to obtain statistically significant results.

To investigate the effect that mechanical force has on the relationship between temperature and electric field, we performed the same set of simulations with the molecule experiencing a mechanical pulling force of 1 nN, applied using the External Force is Explicitly Included (EFEI) approach[39–41] as implemented in Q-Chem. The force was applied to the groups indicated by arrows in Figure 1.

For each simulation, we tested whether bond rupture has occurred by measuring the length of the $C-C$ bond. For each simulation that did not experience bond rupture, we calculated the mean bond length of the scissile bond along the simulation trajectory. To obtain the amplitude of the bond's vibration, we calculated the mean difference between the peak of each oscillation and the mean bond length. For each set of ten simulations with identical parameters, these values were averaged to obtain a given mean bond length and mean vibration amplitude.

3 Results and Discussion

All molecules are stable across the simulation duration up to electric fields of 0.04 a.u. With no applied mechanical force, they are also stable in electric fields of 0.045 a.u. In stronger electric fields, the molecule experiences bond rupture along the scissile bond within a few C−C bond vibrations in every performed simulation. These results agree with previous observations showing that applying mechanical force to a molecule in an external electric field reduces the stability of molecules.[24] As this behaviour was observed regardless of the simulated temperature, we can additionally determine that the stability of the mechanophore's scissile bond in an electric field is independent of thermal conditions, up to temperatures where organic molecules decompose in real-world experiments regardless of any electric field, an effect which is not observable here owing to the short time span of the simulations.
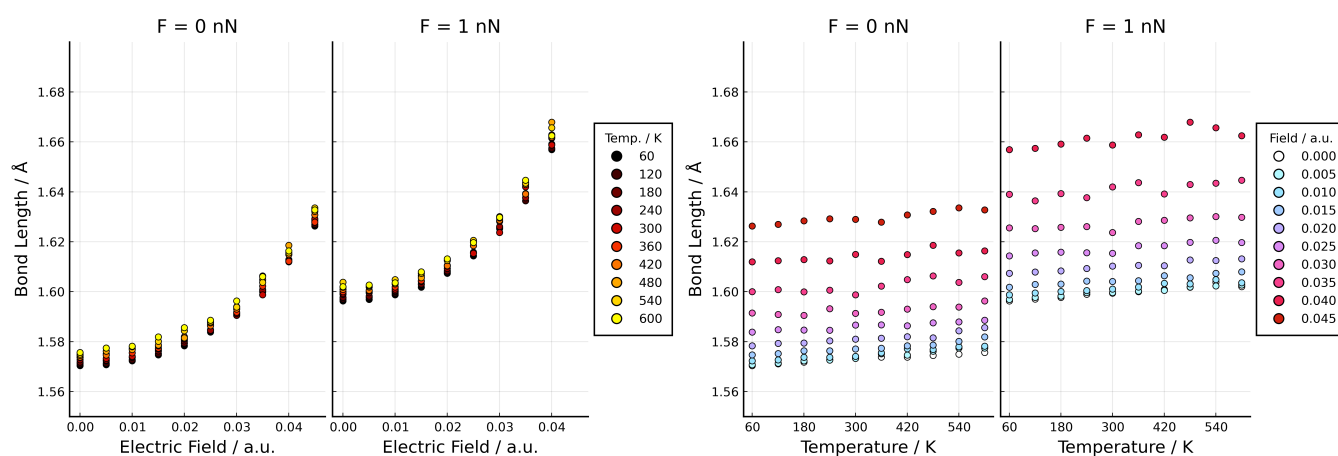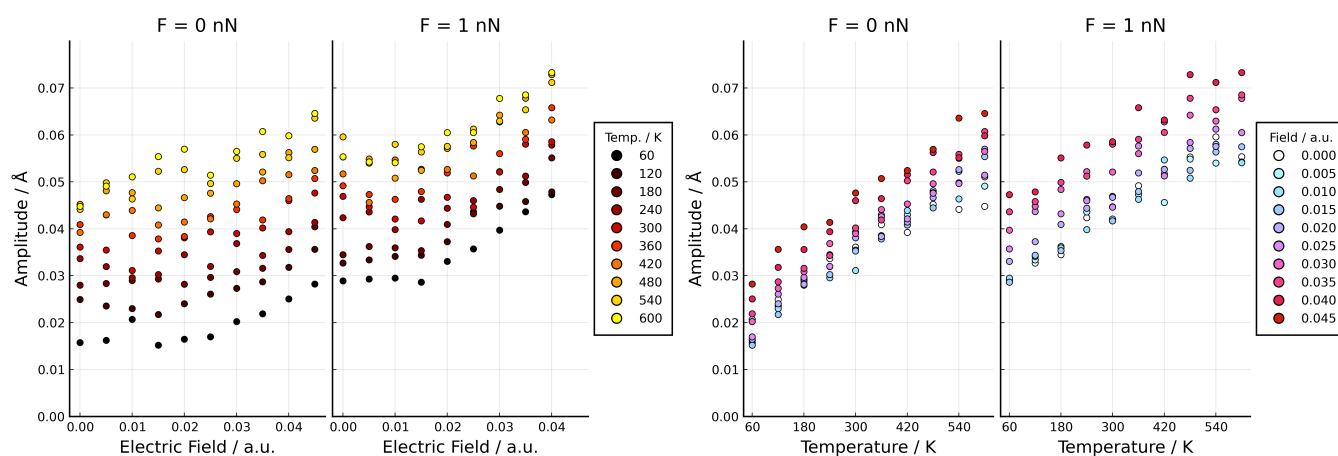

Figure 2: *Mean bond length of the scissile bond of the model mechanophore for different electric fields at different simulation temperatures. The left and right hand side display the same data on different x axes. Each is shown without and with applied mechanical force of 1 nN.*

Figure 2 shows the temperature-induced variation in the mean length of the scissile bond at different electric fields. While the mean C−C bond length increases continuously in stronger electric fields, we find that the magnitude of this increase is independent of the temperature of the system. The spread in mean bond length at different temperatures is small; looking at the change in bond length along the temperature axis shows no significant slope. Strong electric fields causing covalent bonds

to lengthen is a well-known effect,[1] and this lengthening being independent of the temperature shows that effects of OEEFs on bond lengths observed in time-independent electronic structure calculations can be assumed to apply in thermal conditions as well, at least within the time frame considered in our simulations.

Applying mechanical force to the molecule during the simulation increases the overall length of the bond by between 0.02 Å and 0.04 Å compared to the length with no applied force. Applying mechanical force amplifies the lengthening of the bond with electric field strength. Without mechanical force, the scissile bond is on average 0.04 Å longer in an electric field of 0.04 a.u. compared to the bond length at no applied field. With applied mechanical force, this lengthening increases to 0.06 Å. This observation is in agreement with previous findings showing reduced rupture forces of mechanophores in strong electric fields.[24] This increase of the mechanophore's C−C bond length is also independent of the system temperature. Within the tested temperature range, no difference could be observed between low and high simulation temperatures.

Figure 3: *Mean bond vibration amplitude of the scissile bond of the model mechanophore for different electric field strengths at different simulation temperatures. The left and right hand side display the same data on different x axes. Each is shown without and with applied mechanical force of 1 nN.*

The effect of electric field strength and temperature on the scissile bond's vibration amplitude can be found in Figure 3. Here, both the electric field and the temperature show an effect. The amplitude increases with increasing temperature as expected.

Notably, the amplitude also increases with increasing electric field strength. Though not continuous,

there is a clear trend towards higher bond amplitudes in stronger electric fields. We expect that a larger sample size of oscillations for each data point, meaning significantly longer simulation times, would reveal a continuous increase. This increase, too, is in agreement with the observation that bonds generally weaken in strong electric fields. Weaker, longer bonds are more strongly affected by thermally induced atomic motion. This can be seen by the amplitudes for different electric fields being more spread out at higher temperatures. At 60 K, the difference between the amplitude without an electric field and the amplitude at 0.04 a.u. is just over 0.01 Å, while at 600 K, it is close to 0.02 Å.

Applying mechanical force significantly increases the vibration amplitude at low temperatures, but has a much smaller effect at higher temperatures. The amplitudes do not differ significantly between the simulations with and without force at high temperatures. This leads to amplitudes overall being closer to the high-temperature values. This behaviour has not been previously reported in literature. We hypothesize that at low temperatures, the stretching of the molecule increases the effect that the thermal energy has on the atomic motion of the central carbon atoms by increasing the distance between the central carbon atoms and the other carbon atoms along the stretching coordinate, giving the central atoms more space to vibrate. At high temperatures, this effect is no longer relevant as the atoms have enough thermal energy to reach the same vibration amplitudes without mechanical force.

The effect appears to be independent of the electric field strength. The trend of stronger electric fields causing increased vibration amplitudes is also observed when mechanical force is applied, but the higher spread at high temperatures can no longer be observed. Low temperatures also show a higher spread here, as weakening the bond through the application of mechanical force complements the weakening caused by the OEEF, as discussed previously.[24]

4 Conclusions and Outlook

To summarize, we used AIMD simulations of a model mechanophore in an OEEF at different system temperatures to investigate the effect that thermal oscillations and an electric field have on the scissile bond when combined, with and without the additional influence of mechanical pulling force applied to the mechanophore. We found that the bond lengthening caused by the electric field is largely independent of the system temperature. The increase in bond length when mechanical force is applied also does not change with increasing temperature. The bond vibration amplitude changes both with increasing electric field strength and increasing temperature. Applying mechanical force significantly increases the vibration amplitude at low temperatures, but not at high temperatures.

We conclude that investigations of a mechanophore's scissile bond using AIMD simulations can safely be performed in strong electric fields at various temperatures. This is of particular interest for the application of mechanical force to mechanophores in an electric field while considering the realistic thermal vibrations of molecules. As the time span covered by our simulations is short, it is possible that there are dynamical effects that were not observed in this work. A future investigation using simulation methods with lower computational cost would be of interest here, though care must be taken that they are able to correctly describe the effects of mechanical force and electric fields on the mechanophore's electronic structure. On the time scale used in AIMD simulations, this is of no concern, enabling future research into mechanically induced reactions in electric and thermal environments.

5 Acknowledgements

6 Conflicts of Interest

The authors declare no conflicts of interest.

7 Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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